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Electron-rich Carbon Nanorings as Macrocyclic Hosts for Fullerenes†

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Electron-rich cycloparaphenyleneacetylenes as well as their twin "glasses-like" conjugates form stable complexes with fullerenes.

Host molecules of fullerene have been intensively investigated in recent years for roles as separators of specific fullerenes as well as building blocks of well-ordered fullerene-based nanostructures.[1] After the discovery of the complexation of fullerenes with azacrown compounds[2] and γ-cyclodextrin,[3] a range of host molecules for constructing fullerene-containing electroactive nanomaterials has been developed.[1a-d] Because fullerene is a π-conjugated spherical molecule, convex-concave π-π interactions between a fullerene and a π-conjugated tube-like structure have also been envisioned to form much more stable complexes. In fact, it was found that fullerenes can be included inside single-walled carbon nanotubes (SWNTs).[4] After this intriguing study, two examples of host-guest complexes of fullerene with carbon nanorings (CNRs), π-conjugated hydrocarbon macrocycles such as [6]cycloparaphenyleneacetylene ([6]CPPA)[5] and [10]cycloparaphenylene,[6] were reported (Fig. 1). Most recently, the synthesis of SWNTs with perfectly defined diameters as well as their fullerene-included peapods from [n]cycloparaphenylenes has aroused much interest.[7-11] Although much attention has been paid to the properties of clusters consisting of multiple CNR-fullerene complexes, there are no examples of complexes of fullerenes with two or more CNR conjugates. The inclusion properties of [6]CPPA revealed both experimentally[5,12] and theoretically[13] prompted us to investigate a conjugate of two [6]CPPAs for inclusion of fullerenes.

Recently, we reported the efficient synthesis of strained pyridine-containing macrocycles via a tin-mediated reductive aromatisation reaction.[14] A cross-coupling and reduction sequence for [6]CPPA precursors allowed us to find the [6]CPPAs formation via tin-mediated reduction of 1,4-methoxycyclohexa-2,5-diene moieties (Scheme 1). Furthermore, this approach is applicable to synthesis of "glasses-like" twin CNRs, in which two [6]CPPA moieties are covalently joined by a phenyl ring (Fig. 2).[15] Here, we report the complexation of fullerenes with anthracene-containing [6]CPPAs and twin CNRs synthesised via the new synthetic approach.

The D_{3h} symmetric CNR precursors **1** were synthesised from *cis*-9,10-diethynyl-9,10-dimethoxy-9,10-dihydroanthracene with the corresponding *p*-diiodobenzene by means of palladium and copper catalysts (see the Electronic Supplementary Information (ESI)).[16] Subsequently, the tin-mediated reductive aromatisation of CNR precursors **1** with one equivalent of fullerene was carried

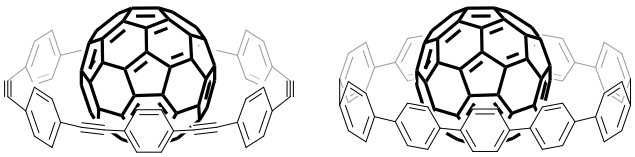
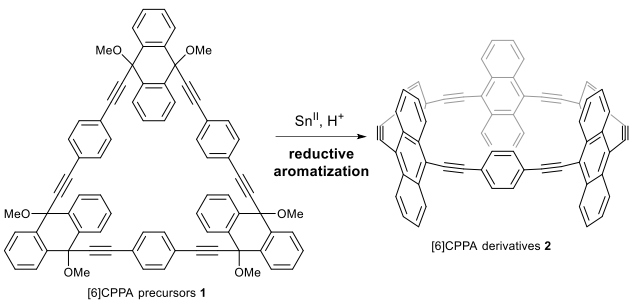


Fig. 1 Reported 1:1 complexes of π-conjugated CNRs and fullerene.



Scheme 1 Synthesis of anthracene-containing [6]CPPA by reductive aromatisation.

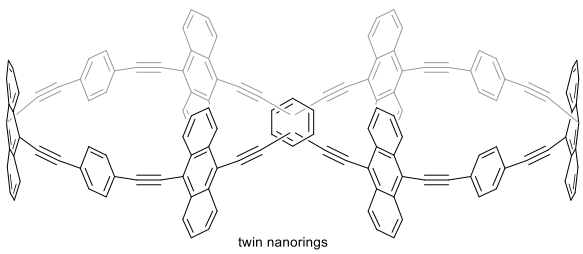
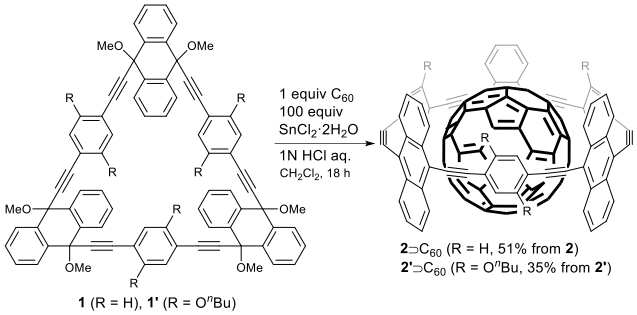


Fig. 2 Twin CNRs as hosts for fullerenes.

out (Scheme 2). After the reduction, the corresponding CNR–fullerene complex **2**⊃C_{60} was successfully isolated in 51% yield.[17] The reductive aromatisation of **1′** bearing electron-donating butoxy groups proceeded smoothly to afford the complex **2′**⊃C_{60} in 35% yield. The CNR–fullerene complexes **2**⊃C_{60} and **2′**⊃C_{60} in the solid state are stable in the dark, but those in solution are not stable, especially under air. In the measurement of variable temperature (VT) ^{1}H NMR of **2**⊃C_{60} (-90 °C to 30 °C in CD_2Cl_2), no temperature-dependent signal separations were observed (concentration: 8.2×10^{-4} mol·dm^{-3}).[18] Because no notable signals of free host **2** were observed using ^{1}H NMR, even at low temperature, the association constant (K_a) of **2**⊃C_{60} is estimated to be larger than 5×10^6 dm^3·mol^{-1} by considering the concentration



Scheme 2 Reductive aromatisation of CNR precursors **1** with fullerene.

of **2**⊃C_{60} and the detection limit of the free host.[19]

Because we established the new synthetic route to obtain stable CNR-fullerene complexes, we focused our attention on twin CNR-fullerene complexes generated from twin CNR precursors **3** (Fig. 3). Although the twin CNR precursor **3a** was not obtained, the double macrocyclization of **4** with diiodide **5a** afforded twin CNR precursors **3b** and **3c** in 11% and 9% yields, respectively (Scheme 3).[20] Instead, precursors **3a** and **3a′** bearing butoxy groups were selectively prepared via a stepwise coupling reaction of **6** with **5a** or **5a′** (Scheme 4). With CNR precursors **3a** and **3a′** in hand, we carried out the synthesis of a complex of twin CNRs with two fullerene molecules. Although twin macrocycles **3b** and **3c** did not afford 1:2 complexes with fullerene,[21] **3a** and **3a′** underwent reductive aromatisation in the presence of excess amounts of fullerene to afford 1:2 complexes of twin CNRs **7** and **7'** with fullerene (Scheme 5). The complex **7**⊃2C_{60} was detected by matrix assisted laser desorption/ionization–time of flight (MALDI–TOF) mass spectroscopy (Fig. S4 in the ESI), but unfortunately could not be isolated successfully. This might be caused by its low stability. When one fullerene molecule interacts with one of two CNRs in **7**, the electron density of another CNR is decreased by charge transfer interaction. Therefore, the second complexation of 1:1 complex **7**⊃C_{60} with fullerene gave the unstable 1:2 complex **7**⊃2C_{60}, which in fact was detectable by mass spectroscopy just after the reduction but decomposed under purification. Instead, a 1:2 complex **7′**⊃2C_{60} bearing butoxy substituents on the CNRs was isolated in 79% yield, and its isotropic patterns was confirmed by MALDI-TOF mass spectroscopy (Figs. S5 and S6 in the ESI). Furthermore, bis(ethoxycarbonyl)methanofullerene (**mC_{60}**)[22] could be included inside twin CNRs **7′** to form the corresponding **7′**⊃2**mC_{60}** (Figs. S7 and S8 in the ESI).[23] These results suggest that the charge transfer interaction between electron-accepting fullerenes and twin CNRs **7′** having electron-donating butoxy groups might stabilise the 1:2 complexation. Because no significant changes were observed in VT ^{1}H NMR spectra of **7′**⊃2C_{60}, the inclusion of two fullerene molecules with two CNRs was considered to be strong (Fig. S9 in the ESI). It is important to note that the high electron density of **7′** is essential in the formation of their stable 1:2 complexes with fullerene as well as **mC_{60}** molecules.

We carried out cyclic voltammetry of twin CNR-fullerene complex **7′**⊃2C_{60} as well as CNR-fullerene complexes **2**⊃C_{60} and **2′**⊃C_{60} with tetrabutylammonium hexafluorophosphate as the supporting electrolyte in *o*-dichlorobenzene (see the ESI). The cyclic voltammogram of **2**⊃C_{60} exhibits a reversible one-electron

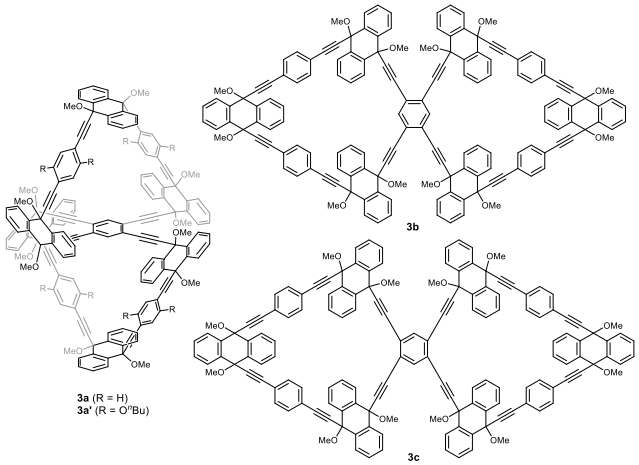
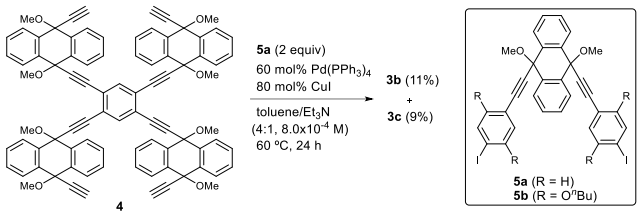
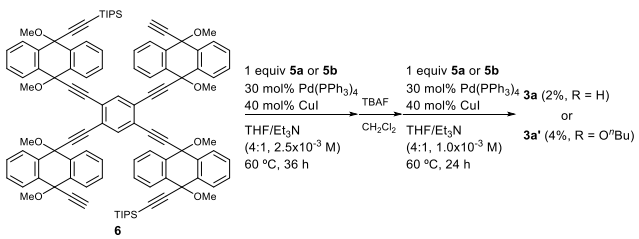


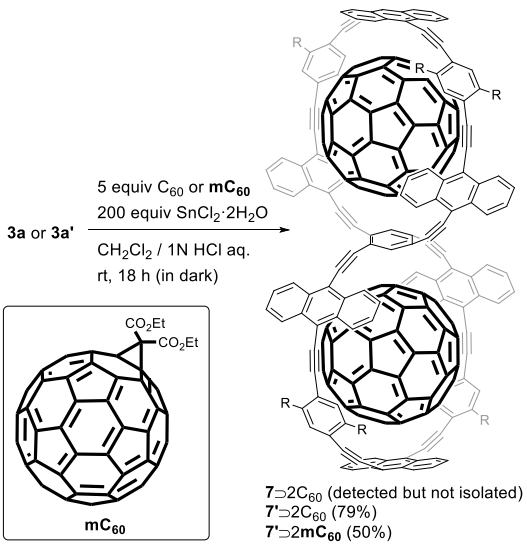
Fig. 3 Twin CNRs precursors **4**.



Scheme 2 Synthesis of twin CNRs precursors **3b** and **3c**.



Scheme 3 Synthesis of twin CNRs precursors **3a** and **3a′**.



Scheme 5 Synthesis of twin CNRs-fullerene complexes.

reduction peak of the fullerene entity at -1.16 V (vs. Fc^+/Fc), which was cathodically shifted by 60 mV as compared with that of pristine fullerene (-1.10 V). With **2′**⊃C_{60}, the peaks retained their

reversible shape and were shifted to a more negative potential (-1.29 V). The first cathodic process corresponding to the reduction of the fullerene entity of **7'**⊃2C_{60} was observed at -1.28 V, which is similar to that of **2′**⊃C_{60}. This difference in cathodic shifts of the reduction potential between these complexes indicates that there is a stronger charge transfer interaction between a fullerene and butoxy-containing CNRs **2′** and **7′**, and that the association constants of electron–rich **2′** and **7′** with fullerenes are larger than that of **2** (K_a >> 5×10^6 $dm^3\cdot mol^{-1}$).[1d, 24] Interestingly, no significant decrement of reversible one-electron redox signals was observed in electrochemical reduction-oxidation cycles in either case.[25] This indicates that the present CNR-fullerene complexes as well as reduced complexes are stable under the measurement conditions.

In summary, we have synthesised π-conjugated CNRs via a cross-coupling and tin-mediated reductive aromatisation sequence. This methodology was applied to the synthesis of more complicated twin CNRs including two fullerene molecules. This is the first example of 1:2 complexation between a π-conjugated hydrocarbon macrocyclic system and two fullerene molecules.[26] We found that the introduction of electron-donating groups on the CNRs significantly enhances the stability of the CNR-fullerene complexes by charge transfer interaction between the CNRs and fullerenes. The complexation of fullerenes with a range of CNR systems will find application in designing buckyball-nanotube structures and investigating their unique function.

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Notes and references

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† Electronic Supplementary Information (ESI) available: experimental details and characterisation data for all compounds. X-ray crystallographic data of **1**, **3b** and **3c**, cyclic voltammograms of **2**⊃C_{60}, **2′**⊃C_{60} and **7′**⊃2C_{60}, and NMR spectra of the new compounds. See DOI: 10.1039/b000000x/

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16 The structure of cyclotrimer **1** was confirmed by X-ray crystallographic analysis. See the SI.

17 CNR–fullerene complexes, **2**⊃C_{60} and **2′**⊃C_{60}, were detectable as 1:1 complexes in high resolution FAB mass spectrometry. See the SI.

18 In the case of **2′**⊃C_{60}, the signals of the methylene protons on butoxy groups separated into two independent peaks below -60 °C. We suppose that this might be caused by the existence of two possible supramolecular isomers of **2′**⊃C_{60} related to the positions of butoxy groups. See the SI.

19 According to the instrument manual, the minimum sample concentration of solute for ^{1}H NMR is usually 4×10^{-4} $mol\cdot dm^{-3}$. Although the detection limit differs according to measuring object, we used this minimum concentration to estimate the equilibrium constant.

20 The structures of twin CNR precursors **3b** and **3c** were confirmed by X-ray crystallographic analyses. See the SI.

21 After the reductive aromatisation of **3b** with 2 equivalents of fullerene, the corresponding twin CNR and their 1:1 complex were detected by MALDI-TOF mass spectroscopy, but 1:2 complex was not observed at all (Figure S9 in the SI).

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25 The irreversible second electron reduction peaks of **2**⊃C_{60}, **2′**⊃C_{60} and **7′**⊃2C_{60} were observed around -1.50 V.

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